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PREPARATION AND ELECTRONIC PROPERTIES OF SEVERAL MEMBERS OF THE--ETC(U)

FEB 81 B KHAZAI, R KERSHAW, K DWIGHT, A WOLD N00014-77-C-0387

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(6) Preparation and Electronic Properties of Several Members of the System $Fe_{(x/3)}Nb_{(2x/3)}Ti_{(1-x)}O_2$

by

(10) Elijan ~~D.~~ Khazai, Robert R. Kershaw, Kirby K. Dwight ~~and~~ Aaron A. Wold

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PREPARATION AND ELECTRONIC PROPERTIES OF SEVERAL MEMBERS OF THE SYSTEM $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$

by

Bijan Khazai, Robert Kershaw, Kirby Dwight and
Aaron Wold

Members of the series $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$ ($x = 0.1, 0.2, 0.3$) were synthesized and their electrical and magnetic properties studied. Powder diffraction patterns of the products could be indexed on the basis of a tetragonal rutile unit cell. ~~(space group $P4_2/mnm-D^{14}_{4h}$)~~. Measurements of sintered discs at 300K gave resistivity values of the order of 10^6 Ω-cm. Magnetic susceptibility studies lead to an assignment of $Fe^{3+}_{x/3}Nb^{5+}_{2x/3}Ti^{3+}_{x/3}Ti^{4+}_{1-4x/3}O_2$ for the formal valencies of the ions. It appears that the observed high resistivity is the result of disordering of the ions in the rutile structure.

Introduction

A large number of recent publications have described the use of both n-TiO_2 or n-Fe_2O_3 as materials which can be used to prepare anodes capable of converting solar energy into electrical energy. In addition to the low efficiency shown by both materials, there are questions concerning the stability of TiO_2 (1) in the presence of oxygen production at the electrode surface.

Despite its lower optical band gap (2.2 eV), α-Fe_2O_3 is not a photoconductor because of its high resistivity, which results from the presence of iron in only the +3 valence state (2). Attempts to prepare conducting α-Fe_2O_3 resulted in the formation of Fe_3O_4, which reduces markedly the photoresponse.

The rare mineral niobian rutile from Salak, North Malaya, has the reported composition Fe_x(II) $(NbTa)_{2x}$ Ti_{1-x} O_2 (3) and contains both iron and either niobium or tantalum ions substituted for titanium in the MO_6 octahedra.

However, there appears little evidence for the assignment of these reported formal valencies.

As a result of the existence of this mineral, a study was undertaken in order to determine if members of the series $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$ could be prepared and their magnetic and electrical properties determined. From such a study, appropriate values could be assigned to the valencies of the transition metal ions and the electrical properties of these compounds could be related to their structure.

Experimental Section

Members of the system $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$ were prepared by direct combination of Fe_2O_3, Nb_2O_5 and TiO_2 under an argon atmosphere at 1250°C. The Fe_2O_3 was obtained from Johnson-Matthey (Specpure) and the Nb_2O_5 from Kawecki Berylco Industries; TiO_2 was prepared by the slow decomposition of ammonium titanyl oxalate (Johnson-Matthey).

Discs of the products where x = 0.1, 0.2, 0.3 were prepared by pressing aliquots of approximately 150 mg at 90,000 P.S.I. The pressed discs were placed on a platinum strip which was then heated, under argon, in a hollow globar tube furnace to 1250°C at a rate of 85° per hour, and maintained at that temperature for 24 hours. At the end of the sintering process, the discs were cooled at the same rate.

Powder diffraction patterns were obtained with a Philips Norelco diffractometer using monochromated high-intensity $CuK\alpha_1$ radiation (λ = 1.5405 Å). Initially, all products were examined by fast scans at 1° (2θ) per minute in order to determine the presence of obvious impurities. Slow scans at 0.25° (2θ) per minute were obtained for all single-phase samples, and their lattice parameters were determined by least squares analysis of all the peak positions in the range $12° \lesssim 2\theta \lesssim 72°$.

The resistivities of the samples were measured using the Van der Pauw technique. Contacts were made by the ultrasonic soldering of indium directly onto the samples, and their ohmic behavior was established by measuring their current-voltage characteristics.

Magnetic susceptibilities were measured using a Faraday balance (4) over the range from liquid nitrogen to room temperature at a field strength of 10.4kOe. Hondo-Owen (field dependency) plots were also made to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism (5).

Results and Discussion

For the composition range studied (x = 0.1, 0.2, 0.3), both iron and niobium atoms can be substituted for titanium in the rutile structure (space group $P4_2/mnm-D^{14}_{2h}$). The powder diffraction patterns of the products can be indexed on the basis of a tetragonal unit cell. As seen in Table 1, there is a monotonic increase in cell parameters with increasing values of x.

TABLE 1

PRECISION LATTICE CONSTANTS FOR THE SYSTEM $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$

Composition	a(Å)	c(Å)
x = 0	4.594 (1)	2.960 (1)
x = 0.1	4.610 (1)	2.969 (1)
x = 0.2	4.627 (1)	2.977 (1)
x = 0.3	4.646 (1)	2.986 (1)

Magnelli and co-workers (6) have shown that the pure rutile, TiO_2, can be reduced to form nonstoichiometric compositions having shear structures as a result of the formation of $Ti^{3+}(3d^1)$. The $3d^1$ electrons created by the reduction of Ti (IV) to Ti (III), can occupy a partially filled conduction band which gives rise to conductivity.

Resistivity measurements for members of the series $Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$ gave values of the order of 10^6 Ω-cm at 300K. The lack of conductivity indicated a need to determine the actual valencies of the ions present and to correlate these results with the ordering of the ions in the rutile structure.

The results of magnetic measurements for the compositions where x = 0.1, 0.3 are indicated in Figure 1, where inverse susceptibility is plotted vs. temperature. It is clear that both compositions show a Curie-Weiss behavior. As indicated in Table 2, two sets of magnetic couples can be considered.

TABLE 2

MAGNETIC DATA FOR $Fe_{.1}Nb_{.2}Ti_{.7}O_2$ (x = 0.3)

Couple	$C^{theo}_{M\ eq.Fe}$	$C^{exp'tl}_{M\ eq.Fe}$
Fe^{2+}, Ti^{4+}	3.00	4.85
Fe^{3+}, Ti^{3+}	4.75	4.85

The first model assumes magnetic contributions from Fe^{2+} only, since Ti^{4+} is a $3d^0$ ion. This is consistent with the well-known observation that Fe^{3+} is not stable under reducing conditions at elevated temperatures. Assuming a Fe^{2+} - Ti^{4+} couple, a value for the Curie constant for a mole equivalent of iron $C_{M\ eq.Fe}$ = 3.00 can be calculated.

A second possibility is the existence of a $Fe^{3+} - Ti^{3+}$ couple. This leads to a Curie constant of 4.75. This value is in close agreement with the experimental value of 4.85. Hence an assignment of $Fe^{3+}_{x/3}\ Nb^{5+}_{2x/3}\ Ti^{3+}_{x/3}\ Ti^{4+}_{1-4x/3}\ O_2$ can be made for the valencies of the ions in this phase.

The observed high resistivity for the products prepared may be attributed to a random distribution of the ions in the rutile structure. Such disorder prevents the formation of $Ti^{3+} - O - Ti^{4+}$ conduction paths.

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Figure 1

Inverse magnetic susceptibility vs. temperature

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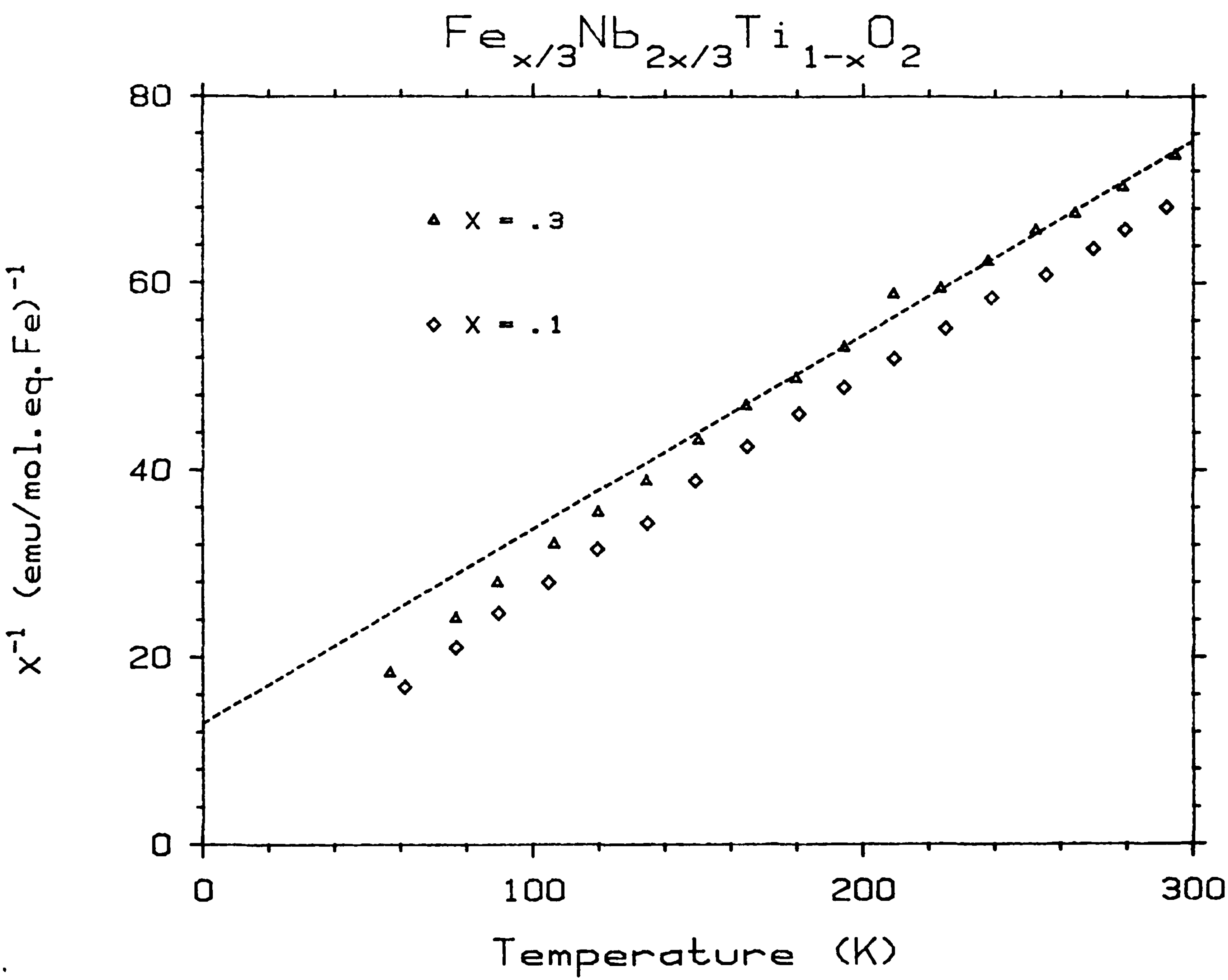
$Fe_{x/3}Nb_{2x/3}Ti_{1-x}O_2$
△ X = .3
◇ X = .1
X^{-1} (emu/mol. eq. Fe)$^{-1}$
0
20
40
60
80
0
100
200
300
Temperature (K)

6

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